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Key Points:
- Miliolacea, high-Mg foraminifera as a proxy for deep ocean conditions
- Mg/Ca values correlate with water temperatures and carbonate ion saturation
- Mg composition of *Pyrgo* sp. calcite is mainly controlled by inorganic processes

Correspondence to:
A. Y. Sadekov,
as2224@cam.ac.uk

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Mg/Ca composition of benthic foraminifera *Miliolacea* as a new tool of paleoceanography

Aleksey Yu. Sadekov[1], Flora Bush[2], Joanna Kerr[1], Raja Ganeshram[2], and Henry Elderfield[1]

[1]Department of Earth Sciences, University of Cambridge, Cambridge, UK, [2]School of GeoSciences, University of Edinburgh, Edinburgh, UK

Abstract The Mg/Ca compositions of benthic foraminifera from the superfamily *Miliolacea* have been studied to explore the use of these high-Mg foraminifera as a proxy for deep ocean conditions. Taxonomic analyses, relative abundance, and depth distributions of different *Miliolacea* species were carried out on a collection of core top samples, covering a depth range of 131 m to 2530 m, along the Australian coast of the Timor Sea. *Pyrgo* sp., composed of *Pyrgo sarsi* and *Pyrgo murrhina*, was found to be the most suitable for proxy studies. Mg/Ca values of this group of foraminifera show a strong correlation with bottom water temperatures and carbonate ion saturation described by the linear relationship: Mg/Ca = 2.53 (±0.22) × BWT + 0.129(±0.023) × $\Delta[CO_3^{2-}]$ + 4.63(±0.53), within the −1°C to 8°C temperature range. Absolute Mg/Ca values of *Pyrgo* sp. calcite and their temperature sensitivity are similar to those observed for inorganic calcite, suggesting that Mg composition of *Pyrgo* sp. calcite is mainly controlled by inorganic processes. The Mg/Ca composition of *Pyrgo* sp. calcite provides a new tool for reconstructing both water temperature and carbonate ion saturation when combined with other proxies for one of these parameters. A down core record from the Eastern Equatorial Pacific has been generated to illustrate how Mg/Ca values can be used for paleoclimate studies. This down core record shows large changes in Pacific bottom waters $[CO_3^{2-}]$ across glacial-interglacial transition, implying an increase in $[CO_3^{2-}]$ during the glacial period.

1. Introduction

Over the last few decades the Mg/Ca composition of planktonic foraminifera has become a well-established proxy for reconstructing past seawater temperatures [e.g., *Anand et al.,* 2003; *Barker et al.,* 2005; *Elderfield and Ganssen*, 2000; *Lea*, 2003]. Mg/Ca thermometry has also been applied to benthic foraminifera, with the aim of understanding the evolution of deep ocean water temperature through time [*Marchitto and deMenocal*, 2003; *Martin et al.,* 2002; *Sosdian and Rosenthal*, 2009]. However, in contrast to planktonic foraminifera, successful applications are rare. One of the challenges facing application to benthic foraminifera is the ability to accurately measure the small changes in Mg/Ca induced by climate variability in benthic foraminifera. For example, *Cibicidoides wuellerstorfi*, the most commonly used benthic foraminifera, has an average Mg/Ca of about 1 mmol/mol at water temperatures of 2°C. Its reported temperature sensitivity lies between 10 and 15% per °C [*Elderfield et al.,* 2006; *Lear et al.,* 2002; *Martin et al.,* 2002; *Tisserand et al.,* 2013]. Therefore, analytical methods capable of accurately determining 0.1–0.15 mmol/mol differences in foraminiferal Mg/Ca values are required to successfully record glacial-interglacial deep water temperature changes in the order of 1°C. This small range in Mg/Ca is close to the typical analytical precision reported in the literature (e.g., one sigma 0.08–0.02 mmol/mol) resulting in a signal-to-noise ratio between 14% and 80% [*Bryan and Marchitto*, 2008; *Elderfield et al.,* 2006; *Sosdian and Rosenthal*, 2009]. In addition, it has been shown that the Mg/Ca of epibenthic foraminifera is also influenced by carbonate ion saturation equivalent to 1.5°C per 10 μmol/kg^2 [*Elderfield et al.,* 2006; *Yu and Elderfield*, 2008]. This significant sensitivity of Mg/Ca values to $\Delta[CO_3^{2-}]$ complicates direct reconstruction of past water temperature using epibenthic foraminifera [*Yu and Elderfield*, 2008] because it requires an independent estimate for $\Delta[CO_3^{2-}]$ values in the past.

In this work we explore the use of high-Mg benthic foraminifera from the superfamily *Miliolacea* as a potential proxy for temperature and $\Delta[CO_3^{2-}]$ of deep water masses. This group is generally characterized by a test wall construction composed of randomly orientated calcite needles with a thin outer covering of parallel crystals, resulting in a distinctive porcelaneous appearance [*Corliss and Honjo*, 1981; *Nooijer et al.,* 2009]. A second identifying characteristic of this family is their relatively high Mg concentration, with Mg/Ca values on average 10 times higher than foraminifera commonly used in paleoclimate reconstructions [*Boyle*, 1983;

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Table 1. Core Top Samples Used in This Study

Name	Latitude	Longitude	Water Depth (m)	Depth Within the Core	BWT (°C)
CD38-17	−1.60	90.43	2580	0–1 cm	1.70
RC15-94	−42.98	20.86	3762	0–1 cm	0.80
RC15-65	−53.07	78.95	4111	4–5 cm	0.95
RC11-120	−43.52	−79.87	3193	5–6 cm	1.54
RC13-275	−50.72	−13.43	1984	0–1 cm	1.16
VM17-92	−62.20	75.12	4087	0–1 cm	0.55
VM27-60	72.18	−8.58	2525	13–15 cm[a]	−0.97
WIND 1B	−35.12	−35.54	4156	0–1 cm	1.14
WIND 3B	−32.64	−48.49	3731	0–1 cm	1.16
WIND 4B	−31.31	−48.50	4570	0–1 cm	0.98
WIND 5B	−31.57	−47.57	3684	0–1 cm	1.26
WIND 6B	−31.27	−47.56	4150	0–1 cm	1.06
WIND 10B	−29.12	−47.55	2871	0–1 cm	1.86
WIND 12B	−25.85	−47.92	4196	0–1 cm	1.00
WIND 22B	−13.61	−51.19	3838	0–1 cm	1.41
WIND 33B	−11.21	−58.77	3520	0–1 cm	1.58
		SO-185 cores–NW Australian margin			
18454	−9.77	131.24	131	0–1 cm	18.30
18472	−11.23	122.98	1947	0–1 cm	2.80
18476	−10.95	120.99	986	0–1 cm	5.20
18478	−11.02	120.08	1769	0–1 cm	x
18480	−12.52	121.65	2295	0–1 cm	x
18481	−12.56	121.84	1897	0–1 cm	x
18482	−12.62	122.15	1508	0–1 cm	x
18483	−12.63	122.31	1356	0–1 cm	x
18484	−12.66	122.37	1247	0–1 cm	x
18485	−12.67	122.41	1132	0–1 cm	x
18487	−12.74	122.62	699	0–1 cm	6.50
18488	−12.89	122.76	555	0–1 cm	7.90
18489	−13.05	122.93	431	0–1 cm	9.00
18491	−13.82	122.99	327	0–1 cm	10.30
18492	−14.14	122.65	350	0–1 cm	x
18496	−12.71	121.3	2530	0–1 cm	1.80
18503	−15.31	121.08	354	0–1 cm	10.40
18506	−15.31	119.5	1525	0–1 cm	x
18507	−13.85	120	2450	0–1 cm	2.00

[a]Sedimentation rate is ~12 cm/ky [*Labeyrie and Duplessy*, 1985]; x used for taxonomy only.

Healey et al., 2008; *Toyofuku et al.*, 2000]. The main aims of this work are to test whether the precision of Mg/Ca thermometry may be improved through use of foraminiferal tests with relatively high Mg concentrations and provide an independent means of estimating past $\Delta[CO_3^{2-}]$. The group *Miliolacea* is relatively new for paleoceanography, and therefore, we used an approach that involved foraminiferal taxonomy, core top calibrations, and a down core glacial-interglacial record.

2. Methods and Materials

Samples were collected during the 2005 RV *Sonne* cruise along three depth transects down the continental slope of NW Australia in the Timor Sea. A multicorer was used to retrieve samples, preserving the undisturbed top sediment layer. Approximately 12 cm^3 of wet sediment was collected for each sample and later wet sieved on 63 μm mesh and dried prior to analyses. At each sample location, in situ temperature, salinity, and pressure were measured using a CTD (Conductivity, Temperature and Depth measurements). The samples, which cover a depth range of 131 m to 2988 m and bottom water temperature (BWT) range of 18°C to 1.7°C, were used for taxonomy studies and calibration of Mg/Ca against BWT.

Foraminiferal taxonomy was investigated in 16 samples from the Timor Sea. All genera of the superfamily *Miliolacea* were picked from >215 μm fraction using a stereomicroscope. Foraminiferal species identification was based on *Loeblich and Tappan's* [1988, 1994] taxonomy. High resolution images of foraminiferal tests were taken using a Philips XL30CP Scanning Electron Microscope at the University of Edinburgh.

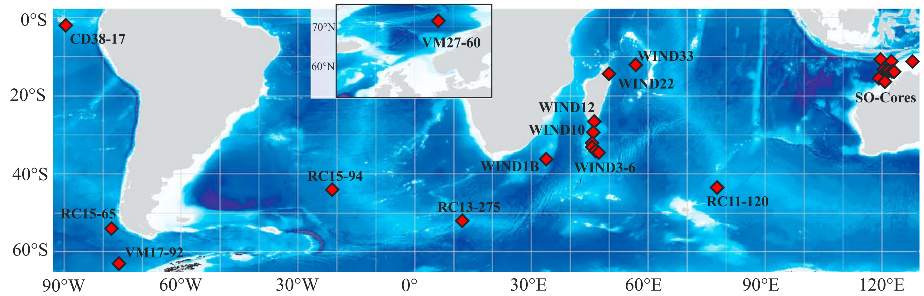

Figure 1. Location of core top samples used for taxonomical study of *Miliolacea* foraminifera (SO-cores) and their Mg/Ca composition (Table 1).

A second set of samples, used only for Mg/Ca calibration, were taken from a large collection of core top samples from our laboratory (Table 1, Figure 1). The samples were selected to cover the temperature range from 1.7 to −1.0°C based on BWT obtained from the World Ocean database [*Locarnini et al.*, 2010].

In addition to core tops, we also used samples from core CD38-17 (RRS *Charles Darwin*) to generate a down core glacial to interglacial record of Mg/Ca values based on *Pyrgo* sp. (for age model and sample preparation, see *Sadekov et al.* [2013]). The $\delta^{18}O$ of *Uvigerina* sp. were measured using a Micromass Optima isotope ratio mass spectrometer and standard lab protocol outlined in *Spero et al.* [2003]. *Uvigerina* sp. samples comprised 5–7 tests picked from size fractions 350–650 μm. Analytical precision was ±0.05%, (±1σ) based on repeat analyses of NBS-19 calcite standard.

Mg/Ca analyses were carried out on foraminiferal samples from 27 core tops (Table 1). All samples were cleaned prior to analyses using standard cleaning protocols [*Barker et al.*, 2003; *Martin and Lea*, 2002] operated by *fOraccle*®, an automatic sample cleaner (more at http://www.geminitechnologyltd.com/foraccle.html), following the procedure described in *Sadekov et al.* [2013].

Mg/Ca measurements were performed using a VISTA-Pro, inductively coupled plasma-optical emissions spectrometer (ICP-OES) following the Ca concentrations matching method described by *de Villiers et al.* [2002] and *Greaves et al.* [2005]. The core top samples from the NW Australian margin each consisted of a single foraminifer test and were therefore run at 1 ppm Ca concentration. The other samples were run at 10 ppm Ca concentration. Measurements were regressed against in-house Mg/Ca ratio standards and Ca concentration standards prepared to cover the range of the samples studied. Consistency standards with matrix matching composition to foraminiferal samples were run every 10 samples to monitor any drift in ICP-OES performance. The analytical precision was assessed using the standard deviations of in-house reference solutions with Mg/Ca ratio 4.17 and 5.17 mmol/mol and was 0.04 mmol/mol or ~1% (one sigma). Ratios of Fe/Ca or Mn/Ca and Al concentrations were monitored to assess cleanliness of the samples following *Greaves et al.* [2005]. The ranges of Fe/Ca and Mn/Ca values were between 0.4 and 1.4 mmol/mol and between 0.1 and 0.8 mmol/mol, respectively. Crucially, we found no correlation between these values and measured foraminiferal Mg/Ca ratios. We picked three shells of *Pyrgo* sp. for down core record and 5–9 shells for core top calibration studies, except for core top samples from the NW Australian margin, which all consist of single foraminiferal shell.

3. Results and Discussion

3.1. Distribution of *Miliolacea* Species

Miliolacea species were found over the complete depth range studied (131–2530 m below sea level) and were most abundant in shallow water samples. Fifteen species from the order *Miliolida*, superfamily *Miliolacea*, were identified with only four species *Pyrgo sarsi, P. murrhina, Spiroloculina subimpressa,* and *Triloculina tricarinata* sufficiently abundant for paleoclimate studies (Figures 2 and 3).

Variation in the relative abundance of *S. subimpressa*, *P. sarsi, P. murrhina, T. tricarinata* with water depth is illustrated in Figure 3. *S. subimpressa* was found to be abundant at shallow sites (<500 m depth); however, no tests were found below 700 m. *T. tricarinata* made up ~20% to 30% of the *Miliolacea* species counted at depths ranging from 1500 to 2000 m and almost no tests were found outside of this depth interval. *P. sarsi* tests were

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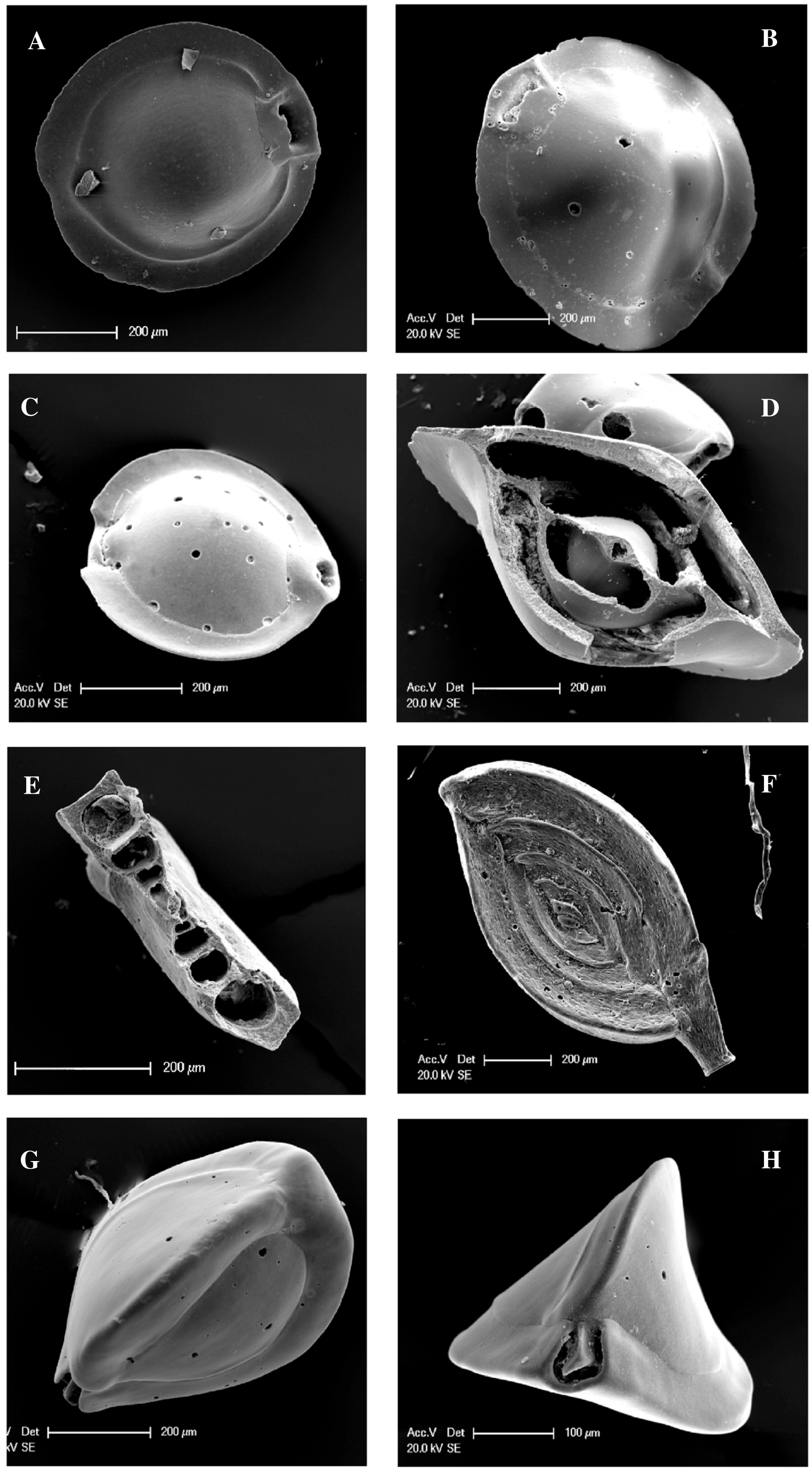

Figure 2. Scanning electron microscope images of: (a and b) *Pyrgo sarsi*; (c) *Pyrgo murrhina*; (d) *Pyrgo murrhina* (biloculine coiling structure—successive chambers are 180° apart [*Loeblich and Tappan,* 1988, 1994]). (e and f) *Spiroloculina subimpressa*; (g and h) *Triloculina tricarinata.*

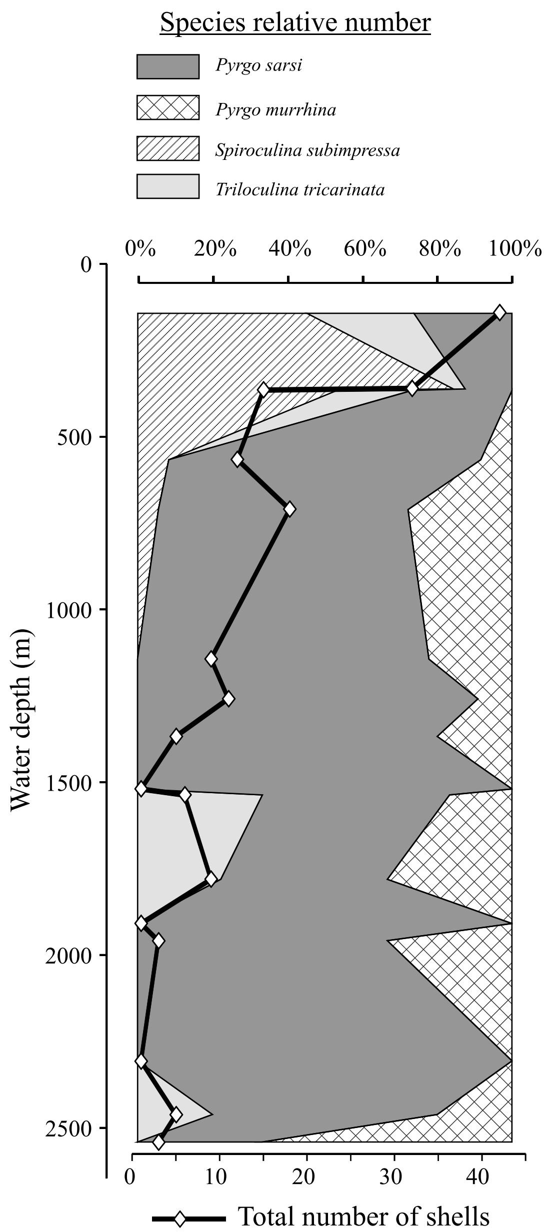

Figure 3. Relative abundance of the four most abundant *Miliolacea* species (*P. sarsi, P. murrhina, S. subimpressa,* and *T. tricarinata*) along a depth transect in Timor Sea, Western Australian Coast. Note the gradual decrease in total numbers of *Miliolacea* tests and the presence of *Pyrgo* sp. along all depth transects from 131 m down to 2530 m.

found in almost every sample over a depth range of 131–2530 m. Although the absolute abundance of *P. sarsi* decreased with increasing depth, it made up >50% of the total population of *Miliolacea* species counted between 400 m and 2500 m. Below 2500 m *P. murrhina* became the dominant species in the *Miliolacea* assemblage (e.g., 67% of the total counts). *P. murrhina* tests were not found above 500 m. Its abundance remained low (on average, one test per sample) below 500 m. These observations are generally consistent with previous studies [*Corliss and Honjo*, 1981; *Haynes*, 1981; *Murgese and De Deckker*, 2005; *Murray*, 2006], which suggest that the distribution of these benthic foraminifera is controlled by bottom water oxygen levels and the organic matter content of sediments. *Pyrgo*, an opportunistic and strictly epifaunal genera, is found most abundantly in well-oxygenated waters with a low carbon flux and is therefore prevalent in bathyal-abyssal zones of the ocean [*Geslin et al.,* 2004; *Gooday*, 2003; *Murgese and De Deckker*, 2005; *Rathburn and Corliss*, 1994].

Depth distribution of *Miliolacea* species restricts their application in paleoclimate studies. For example, *S. subimpressa* is found to be most suited for use in shallow water studies (0–300 m deep) whereas *Pyrgo* sp. (*Pyrgo* sp. = *Pyrgo sarsi* + *Pyrgo murrhina*) is more suited to deep water studies (>400 m). We suggest that based on its ecology, global distribution, and relatively high abundance, *Pyrgo* sp. could be a suitable analog to *Cibicidoides wuellerstorfi,* which is currently used in paleoclimate studies. *Pyrgo* sp. has also been reported across most of the oceans from as early as the Eocene [*Bandy and Arnal*, 1957; *Gudmundsson*, 1998; *Kovács and Arnaud-vanneau*, 2004; *Levy et al.,* 1998; *Luczkowska*, 1972], supporting its use as potential proxy carrier.

3.2. Mg/Ca Composition of *Miliolacea*

Mg/Ca compositions were only measured for species of the three most abundant genera: *Pyrgo, Spiroloculina*, and *Triloculina*. Average Mg/Ca values for the shallowest core top sample with BWT 18.3°C are 88.4 mmol/mol, 94.1 mmol/mol, and 98.4 mmol/mol for *Pyrgo sarsi, S. subimpressa*, and *T. tricarinata,* respectively (Figure 4). Consistent with previous studies, these Mg/Ca values are considerably higher than those in other benthic species [*Healey et al.,* 2008].

We measured Mg/Ca values of individual tests of *S. subimpressa*, *P. sarsi, P. murrhina,* and *T. tricarinata* species in two core top samples to assess intergenera and interspecies variability (Figure 4). At the shallowest core top sample from BWT of 18.3°C, *P. sarsi* shows the largest standard deviation, 7.7 mmol/mol (or ~9% relative standard deviation (RSD)). *T. tricarinata* and *S. subimpressa* show standard deviations of only 2.9 mmol/mol (~3% RSD) and 3.3 mmol/mol (~4% RSD), respectively. At the core top sample from BWT of 6.5°C, *P. sarsi* Mg/Ca variability is 2.78 mmol/mol (1σ and ~11% RSD) with a mean value of 24.8 mmol/mol exceeding *P. murrhina*

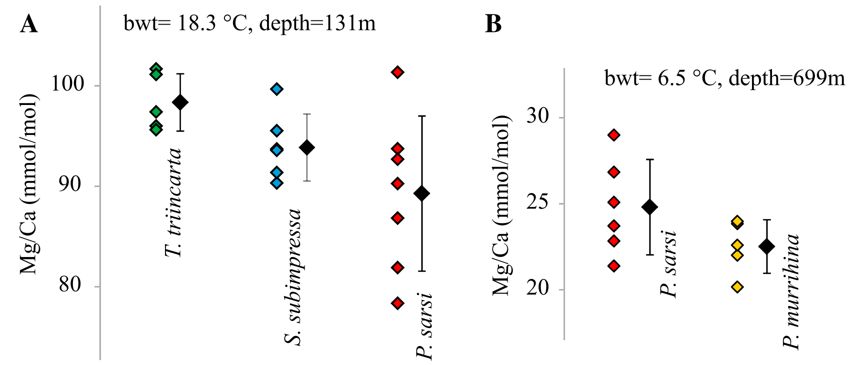

Figure 4. Intratest variability of Mg/Ca composition of the four most abundant *Miliolacea* species (*P. sarsi*, *P. murrhina*, *S. subimpressa*, and *T. tricarinata*) in two core tops from water depths of (a) 131 m and (b) 699 m. Colored diamonds are Mg/Ca values for individual foraminifera tests. Black diamonds are mean Mg/Ca values for each species. Error bars are ±1σ. The mean Mg/Ca values for all species are similar within ±1σ error interval.

(1.56 mmol/mol (1σ and ~7% RSD)), which shows a mean value of 22.5 mmol/mol. We used *t*-test to compare whether the difference between Mg/Ca values of these species is statistically significant. It showed that only the difference between *T. tricarinata* and *Pyrgo* sp. at the warmer site is statistically significant at 95% confidence interval (*p* values is 0.033). Tests of *S. subimpressa* and *T. tricarinata* also have slightly higher Mg/Ca values and significantly smaller inter-test variability. This minimal intergenera difference contrasts with known variability in low-Mg foraminifera which vary significantly not only between genera but also between species of one genus [*Healey et al.,* 2008; *Tisserand et al.,* 2013; *Yu and Elderfield*, 2008]. *Miliolacea* is a relatively ancient group within the foraminiferal phylogeny, and it has been suggested that it has minimal control on Mg incorporation into foraminiferal calcite compared with the more evolutionary advanced groups of foraminifera with low Mg calcite [*Nooijer et al.,* 2009; *Pawlowski et al.,* 2003]. Minimal biological control on Mg incorporation into calcite is also supported by relatively high Mg fractionation coefficient ($D_{Mg} = Mg/Ca_{calcite}{:}Mg/Ca_{seawater}$), which range from 0.005 to 0.018 at 6.5°C and 18.3°C, respectively (Figure 4). The range of these values overlap with that of D_{Mg} reported for inorganically precipitated calcite (e.g., 0.012–0.027) supporting a dominance of inorganic processes during *Miliolacea* calcite precipitation [*Mucci and Morse,* 1983; *Oomori et al.,* 1987]. Therefore, we suggest that species *P. sarsi* and *P. murrhina* can be combined (i.e., *Pyrgo* sp.) to increase the total number of tests per sample for paleoclimate studies and reduce the effect of intraspecies Mg/Ca variation. It is also possible that the other *Miliolacea* genera can be included together with *Pyrgo* sp., although this assumption would require additional conformation by future studies.

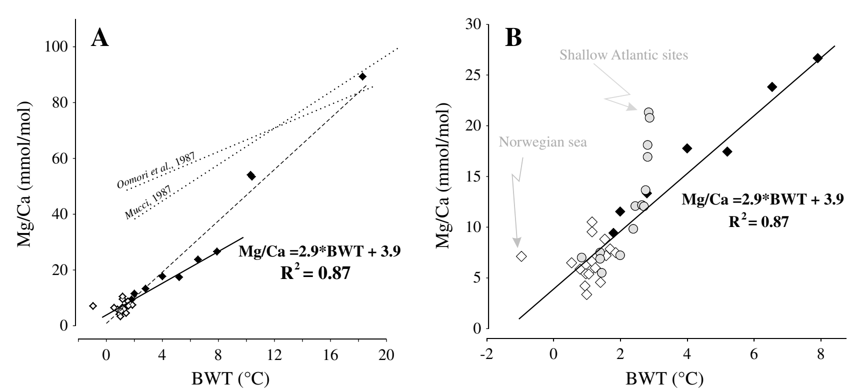

Figure 5. Calibration of *Pyrgo* sp. Mg/Ca values against bottom water temperatures (a) from −1 to 20°C and (b) from −1 to 8°C. Solid diamonds are Mg/Ca values for samples from Timor Sea depth transect (Table 1). Open diamonds are Mg/Ca values for core top samples from the other core top samples (Table 1). Dashed line is linear regression through all data set (Figure 5a). Solid line is the linear regression through Mg/Ca values within −1 to 8°C temperature range (Figure 5b). Dotted lines are temperature dependence of Mg/Ca values of inorganic calcite reported by *Mucci* [1987] and *Oomori et al.* [1987] (linear regression assumed). Note the similar slopes of temperature dependence of Mg/Ca values in *Pyrgo* sp. and inorganic calcite. Grey dots are *Pyrgo* sp. mean Mg/Ca values from *Healey et al.* [2008].

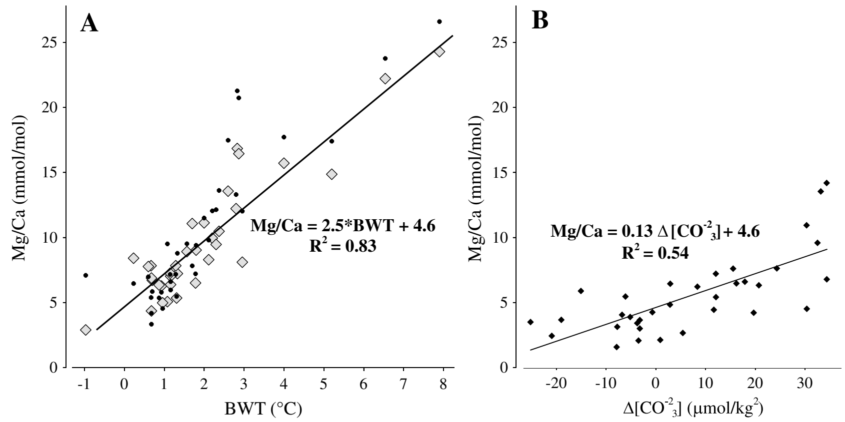

Figure 6. Result of multiple linear regressions of *Pyrgo* sp. Mg/Ca composition against bottom water temperatures and carbonate ion saturation, $\Delta[CO_3^{2-}]_{calcite}$. (a) Temperature component of the multiple regression. Black dots represent the original mean Mg/Ca values for each station combined with *Pyrgo* sp. data from *Healey et al.* [2008], same as in Figure 5b. Grey diamonds are Mg/Ca values corrected for $\Delta[CO_3^{2-}]$ effect ($Mg/Ca_{corrected} = Mg/Ca_{original} - 0.13 \times \Delta[CO_3^{2-}]$). Note reduction in deviation of corrected Mg/Ca values from regression line (solid line) especially for shallow Atlantic sites and the site from Norwegian Sea (Figure 5b). (b) Carbonate ion saturation component of the multiple regression. Black diamonds are Mg/Ca values corrected for temperature effect ($Mg/Ca_{corrected} = Mg/Ca_{original} - 2.53 \times T$). Linear regression (solid line) only approximates the relationship, which is most likely nonlinear above $\Delta[CO_3^{2-}]$ values of ~20 μmol/kg^2.

3.3. Mg/Ca Calibration Against Bottom Water Temperature and Carbonate Ion Saturation

Mg/Ca values of *Pyrgo* sp. have a strong positive correlation with BWT (Figure 5a). Linear regression fit best into the observed data set with slope of 4.6 ± 0.2 and intercept of 0.97 ± 1.07, giving R^2 values of 0.9. The majority of the sites from deeper locations (<8°C) fall on a slightly different regression line with slope of 2.85 ± 0.24 and intercept of 3.89 ± 0.66 (Figure 5b). Close examination also reveals that the higher Mg/Ca values of shallow water samples, as well as samples from Norwegian Sea, deviate from the rest of the data set (Figure 5b). Similar elevated Mg/Ca values have previously been reported for other epibenthic foraminifera from the Norwegian Sea and have been attributed to the effect of carbonate ion saturation ($\Delta[CO_3^{2-}]$) on foraminiferal Mg/Ca values [*Yu and Elderfield*, 2008]. This is particularly prominent in the Arctic Basin where bottom waters are close to freezing point but have a high carbonate ion concentration. Although the origin of the $\Delta[CO_3^{2-}]$ effect on foraminiferal Mg/Ca values is still unknown (see more in *Allen and Hönisch* [2012]), it has been shown to have a sensitivity of ~ 0.09 mmol/mol, or 1.5°C equivalent per 10 μmol/kg^2 [*Elderfield et al.,* 2006]. To decouple the temperature component from $\Delta[CO_3^{2-}]$, we used multiple linear regression of Mg/Ca values against BTW and $\Delta[CO_3^{-2}]$ following *Elderfield et al.*'s [2006] approach. We used averaged Mg/Ca values for each station and also included Mg/Ca values of *Pyrgo* sp. from *Healey et al.* [2008] (Figure 6). We also limited our temperature range to −1 to 8°C to avoid any potential error in temperature or $\Delta[CO_3^{2-}]$ due to proximity to water column thermocline (e.g., <500 m). The combined regression is described by the following equation:

$$Mg/Ca = 2.53(\pm 0.22) \times BWT + 0.129(\pm 0.023) \times \Delta\left[CO_3{}^{2-}\right] + 4.63(\pm 0.53), \quad R^2 = 0.87 \tag{1}$$

The largest factor controlling Mg/Ca values in our data set is temperature, with a sensitivity of ~2.5 ± 0.2 mmol/mol per °C (Figure 6a). The $\Delta[CO_3^{2-}]$ effect is less pronounced, with a sensitivity of ~ 1.3 ± 0.2 mmol/mol or 0.5°C equivalent per 10 μmol/kg^2 (Figure 6b). Therefore, Mg/Ca sensitivity of *Pyrgo* sp. calcite to $\Delta[CO_3^{2-}]$ is much smaller compared to that reported for other epibenthic foraminifera (e.g., 0.5°C versus 1.5°C equivalent per 10 μmol/kg^2 for *Pyrgo* sp. and *Cibicidoides* sp. accordingly) [*Elderfield et al.,* 2006]; nevertheless, it is not negligible. The $\Delta[CO_3^{-2}]$ effect is critical for paleoclimate reconstructions where small changes in temperature are accompanied by a significant modification of the carbonate system [*Yu and Elderfield*, 2008]. For example, $[CO_3^{2-}]$ and therefore $\Delta[CO_3^{2-}]$ has decreased by ~30 μmol/kg^2 in the Atlantic Ocean intermediate water masses since the last glacial maximum (LGM) [*Yu et al.,* 2013], which would underestimate temperature change during this period by ~ 1.5°C. The relationship between *Pyrgo* sp. Mg/Ca values and $\Delta[CO_3^{2-}]$ is probably not linear above ~20 μmol/kg^2 (Figure 6b). Large deviations of the two most shallow samples from Timor Sea also suggest that the effect of $\Delta[CO_3^{2-}]$ is much stronger at higher carbonate ion saturation values (Figure 5a). Our data set has only few samples from this range of carbonate ion saturations and therefore insufficient to accurately describe the relationship of Mg/Ca values and $\Delta[CO_3^{-2}]$ above values of ~20 μmol/kg^2.

The temperature sensitivity of ~ 2.5 ± 0.2 mmol/mol per °C for *Pyrgo* sp. Mg/Ca values is similar to both the temperature sensitivity of inorganic calcite [*Mucci and Morse*, 1983; *Oomori et al.,* 1987] and results of culturing experiments using the shallow water *Miliolacea* foraminifera species *Quinqueloculina yabei* [*Toyofuku et al.,* 2000] (Figure 5a). This agreement, together with similar Mg fractionation coefficients for *Miliolacea* calcite, strongly support the idea that this group of foraminifera precipitate their calcite with minimal biological influence on Mg incorporation. Fractionation of Mg stable isotopes in *Pyrgo* sp. calcite is also within the of range inorganically precipitated calcite [*Wombacher et al.,* 2011], highlighting close similarities between *Miliolacea* and inorganically precipitated calcites. It is interesting to note that the absolute Mg/Ca values of *Pyrgo* sp. only overlap with inorganic calcite at shallow sites but are smaller at deep water samples (Figure 5a). Currently, we do not have an explanation for these discrepancies but we hypothesize that it may be related to the mechanism responsible for the effect of $\Delta[CO_3^{2-}]$ on Mg incorporation into calcite. Note that variations of D^{Mg} values reported for inorganic calcite is larger than the difference between D^{Mg} of inorganic and *Pyrgo* sp. calcite [*Katz*, 1973; *Oomori et al.,* 1987].

The relatively high Mg/Ca values of *Pyrgo* sp. allow significant reduction in analytical errors of temperature estimates compared to other species of benthic foraminifera. For example, at a bottom water temperature of 4°C, *Cibicidoides* sp. and *Uvigerina* sp. have Mg/Ca values of ~1.3 and 1.1 mmol/mol [*Bryan and Marchitto*, 2008; *Lear et al.,* 2002], whereas *Pyrgo* sp. has a ratio of ~18 mmol/mol. For comparison, the analytical precision (0.08 mmol/mol, i.e., 2σ) expressed as a percentage of the Mg/Ca ratios of these species are 6% and 7% versus 0.4%, respectively, accounting for about 0.5–1°C for *Cibicidoides* sp. [*Lear et al.,* 2002; *Marchitto et al.,* 2007; *Yu and Elderfield*, 2008], 1°C for *Uvigerina* sp. [*Elderfield et al.,* 2010], and only 0.03°C for *Pyrgo* sp. temperature estimates.

3.4. Application of New *Pyrgo* sp. Mg/Ca Calibration to a Paleocenographic Reconstruction

Tight coupling between the effects of temperature and $\Delta[CO_3^{2-}]$ on *Pyrgo* sp. Mg/Ca values prevents independent reconstruction of one of these parameters in the past. However, this apparent drawback can provide novel ways to reconstruct both parameters if *Pyrgo* sp. Mg/Ca values are combined with Mg/Ca data from other benthic foraminifera. Mg/Ca values of infaunal benthic foraminifera such as *Uvigerina* sp. have been shown to reflect only BWT; therefore, it could be an ideal proxy for decoupling past changes in $\Delta[CO_3^{-2}]$ and BWT [*Elderfield et al.,* 2010]. Alternatively, *Pyrgo* sp. Mg/Ca values can be combined with B/Ca composition of *Cibicidoides* sp. as a proxy for past $\Delta[CO_3^{2-}]$ [*Rae et al.,* 2011; *Yu and Elderfield*, 2007]. To test one of these approaches and also validate our newly obtained calibration (i.e,. equation (1)), we generated a down core *Pyrgo* sp. Mg/Ca record for the last glacial-interglacial transition in the Eastern Equatorial Pacific (core CD38-17, 01°36′04″S; 90°25′32″W, 2580 m) (Figure 7a). We also measured δ^{18}O values of *Uvigerina* sp. from the same site to have an independent estimate of potential changes in BWT (Figure 7b). We combined this data with published Mg/Ca values of *Uvigerina* sp. by *Martin et al.* [2002] from a nearby site (TT163-31, 03°35′S; 83°57′W, 3205 m) (Figure 7c).

At present, both sites (i.e., CD38-17 and TT163-31) are bathed by Circumpolar Deep Water (CDW), a mixture of Antarctic Bottom Water, and North Atlantic Deep Water (NADW) [*Reid*, 1997; *Sigman et al.,* 2010; *Tsuchiya and Talley*, 1996]. There are several paleorecords for this water mass, which estimate a glacial-interglacial temperature change of approximately 2–3°C [*Elderfield et al.,* 2010; *Martin et al.,* 2002]. The history of $\Delta[CO_3^{2-}]$ or $[CO_3^{2-}]$ changes (hereafter, we use concentration due to its relevance for paleoreconstructions) is less well known for CDW, with some authors suggesting a minimal change [*Anderson and Archer*, 2002; *Yu et al.,* 2013] and others inferring elevated $[CO_3^{2-}]$ by ~25 μmol/kg^2 for glacial period [*Rickaby et al.,* 2010]. CDW is by far the largest deep water mass on the planet; hence, our down core application in the Eastern Equatorial Pacific could be also relevant for paleoceanography.

The down core *Pyrgo* sp. Mg/Ca record shows a glacial-interglacial change of ~1.5 mmol/mol (Figure 7a). Mg/Ca values begin to increase at ~18.5 kyr, reaching interglacial values by 15.5 kyr. This general trend in Mg/Ca values has significant variability, which we attribute to either the small number of shells used in the

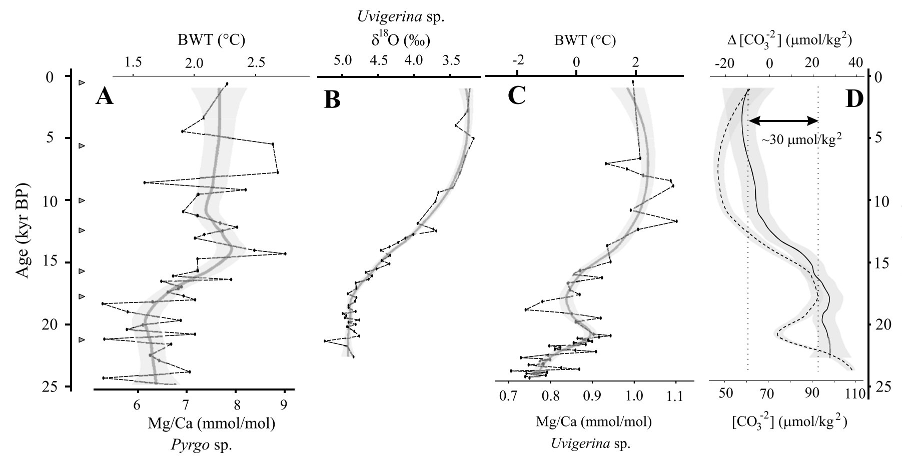

Figure 7. Trial application of *Pyrgo* sp. Mg/Ca values to paleoceanography of Eastern Equatorial Pacific deep waters. (a) Down core record of *Pyrgo* sp. Mg/Ca composition for site CD38-17 (01°36′04″S; 90°25′32″W, 2580 m). Age model is based on seven C^{14} AMS dates (grey triangles) [*Sadekov et al.,* 2013]. (b) Down core record of *Uvigerina* sp. δ^{18}O values. Amplitude of glacial to interglacial change is ~ 1.7‰ and similar to published data for Eastern Equatorial Pacific [*Shackleton,* 2000; *Stott et al.,* 2007]. (c) Mg/Ca values of *Uvigerina* sp. from sediment core located near site CD38-17 [*Martin et al.,* 2002]. The temperature estimates are based on *Elderfield et al.* [2010] temperature calibration for this species. (d) Estimates of changes in $\Delta[CO_3^{2-}]$ and $[CO_3^{2-}]$ values across glacial-interglacial transition. Solid line is based on combination of Mg/Ca values of *Pyrgo* sp. (Figure 7a) and *Uvigerina* δ^{18}O values (Figure 7b). Dashed line is based on combined Mg/Ca values of *Pyrgo* sp. (Figure 7a) and Mg/Ca values of *Uvigerina* sp. from *Martin et al.* [2002] (Figure 7c). Refer to text about calculations of $\Delta[CO_3^{2-}]$ and $[CO_3^{2-}]$ values. For all plots: black circles are original data values, solid thick lines are polynomial regression fittings using weighted least squares method in *R* code package. Grey intervals are ±1 standard error interval of the polynomial regression through the data (read more at www.r-project.org function loess).

analyses (e.g., three shells per sample) or the wide range of sample size fractions (e.g., 250–600 μm) used for Mg/Ca measurements. Changes in *Uvigerina* sp. δ^{18}O values are identical within the error of age model for similar Equatorial Pacific records [*Shackleton*, 2000; *Stott et al.,* 2007] and have an amplitude of 1.7‰ (Figure 7b). The glacial-interglacial change in *Pyrgo* sp. Mg/Ca is equivalent to ~ 0.5°C, if we assume no changes in bottom water $[CO_3^{2-}]$ during this period. Temperature change derived from δ^{18}O of *Uvigerina* sp. on the other hand would imply ~2.5°C (e.g., 1.7‰ = 1.1‰ (global ice volume effect) +0.6‰ local temperature/salinity change with sensitivity of 0.25‰ per °C). The δ^{18}O-based estimate agrees well with previous BWT reconstructions for the CDW [*Martin et al.,* 2002] but ~ 4–6 times smaller than the temperature estimate based on *Pyrgo* sp. Mg/Ca values. Large mismatch between proxies strongly suggests that our initial assumption about constant bottom water $[CO_3^{2-}]$ is incorrect. To estimate the change in $[CO_3^{2-}]$, we used two independent approaches. The first approach was to use BWT derived from *Uvigerina* sp. Mg/Ca data by *Martin et al.* [2002] and include it into our calibration (e.g., equation (1)). We used the original Mg/Ca values of *Martin et al.* [2002] but used *Elderfield et al.* [2010] temperature calibration for this species (Figure 7d, dashed line). The second approach was to estimate BWT by subtracting global ice volume effect [*Waelbroeck et al.,* 2002] from our *Uvigerina* sp. δ^{18}O values and assuming no changes in local salinity (Figure 7d, solid line). The records derived using both approaches show a similar pattern of a large increase in $[CO_3^{2-}]$ during glacial intervals, with a difference of ~30 μmol/kg^2 between Holocene and LGM values. Note that our absolute values of $[CO_3^{2-}]$ changes could be subject to large errors derived from used temperature estimates. For example, *Martin et al.* [2002] suggested that their record of *Uvigerina* sp. Mg/Ca, which we used for BWT, is probably affected by local dissolution. We also assumed that local salinity did not change at site CD38-17 during the last glacial-interglacial transition. Uncertainties in both of these factors would overestimate the absolute change in BWT and, therefore, $[CO_3^{2-}]$ values. On the other hand, the general trend in $[CO_3^{2-}]$ changes across the glacial-interglacial transition clearly suggests elevated $[CO_3^{2-}]$ of CDW during LGM. Increased $[CO_3^{2-}]$ would be consistent with the hypothesis of carbon storage in the deep ocean during glacial periods and support findings of elevated $[CO_3^{2-}]$ in deep waters of Weddell Sea [*Rickaby et al.,* 2010]. Alternatively, large changes in $[CO_3^{2-}]$ at site CD38-17 would suggest a different source of deep Pacific waters at 2.5 km during the glacial period. *Okazaki et al.* [2010] recently proposed that the

Northern Pacific region was a significant source of Pacific deep waters during periods of weak NADW formation in Atlantic Ocean. Formation of carbon-rich deep waters in the Northern Pacific can explain the changes observed in our record but would contradict recent findings of little or no $[CO_3^{-2}]$ change in Western Equatorial Pacific [*Yu et al.,* 2013]. Our down core record is designed for proxy validation rather than accurate reconstruction of past climates; therefore, more $[CO_3^{2-}]$ reconstructions are needed from different depths of the Pacific Ocean to clarify changes in the carbonate system. We also suggest that *Pyrgo* sp. Mg/Ca values can be a new and powerful tool for these studies as well as other research aimed at reconstructing the evolution of past deep water masses in the Cenozoic.

4. Conclusions

The Mg/Ca composition of foraminifera from the superfamily *Miliolacea* can be used as a novel proxy for reconstructing deep ocean temperature. In this study, we showed that *S. subimpressa, T. tricarinata*, *P. sarsi*, and *P. murrhina* were the most abundant *Miliolacea* species, but due to the wide depth range and cosmopolitan distribution, *Pyrgo* sp. (*P. sarsi* + *P. murrhina*) offer the most potential as proxy for paleoreconstruction. Mg/Ca values of *Pyrgo* sp. strongly correlate with bottom water temperatures and carbonate ion saturation, showing ~2.5 mmol/mol increase per °C or per ~20 μmol/kg^2 change in $\Delta[CO_3^{2-}]$ values. Both absolute Mg/Ca values of *Pyrgo* sp. calcite and their temperature sensitivity are similar to values observed for inorganic calcite. This close similarity, together with previous findings, strongly advocates that the Mg composition of *Pyrgo* sp. calcite is governed primarily by inorganic processes and is unique among other foraminifera. Due to its high Mg/Ca values, *Pyrgo* sp. also offers a significant reduction in the analytical error of temperature estimates compared to other benthic foraminifera. We applied our new *Pyrgo* sp. Mg/Ca calibration on a down core record to reconstruct past BWT and $[CO_3^{2-}]$ in the Eastern Equatorial Pacific. The record clearly shows glacial-interglacial transition with a major shift in *Pyrgo* sp. Mg/Ca values between 18.5 and 15 kyr. Combined with temperature estimates from published *Uvigerina* sp. Mg/Ca values [*Martin et al.,* 2002], our down core record suggests that glacial deep waters had an elevated $[CO_3^{2-}]$ compared to Holocene values. In summary, we suggest that the Mg/Ca composition of *Pyrgo* sp. offers a new and powerful tool for studying Cenozoic paleoceanography, especially when combined with other proxies of deep ocean waters.

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